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# The Relaxation between Pore Water Chemistry and Benthic Fluxes of Nutrients and Manganese in Narragansett Bay, Rhode Island

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# The relation between pore water chemistry and benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island

*Richard J. McCaffrey*
Graduate School of Oceanography, University of Rhode Island, Kingston 02881

*Allen C. Myers*[1], *Earl Davey, and George Morrison*
Environmental Research Laboratory, Kingston, Rhode Island 02881

*Michael Bender, Nile Luedtke, Douglas Cullen, Philip Froelich, and Gary Klinkhammer*
Graduate School of Oceanography, University of Rhode Island

*Abstract*

Benthic fluxes of dissolved nutrients and manganese from biologically disturbed, relatively unpolluted sediment in Narragansett Bay, Rhode Island, have been measured. Analyses of the vertical gradients of chemical species dissolved in pore waters and the uptake of $^{22}Na$ from the overlying water permits evaluation of the contribution of biological advection and molecular diffusion to the transport of dissolved materials across the sediment–water interface. The activity of bottom-dwelling organisms appears to be about as important as molecular diffusion in most cases. The sum of the independently estimated contributions by both mechanisms is in good agreement with integrated benthic fluxes measured in situ. Sulfate and oxygen oxidize comparable amounts of organic matter in these sediments.

Benthic nutrient fluxes are important in the nutrient balance of many aquatic systems. Migration out of sediments supplies about 80% of the nutrients entering Narragansett Bay during certain times of year (Hale 1974; Nixon et al. 1976). Release of nutrients from sediments is largely regulated by the rates at which organic detritus reaches the sediment, the rates at which this detritus is decomposed (mainly by bacteria), and the rates at which nutrients released to pore waters are transported to the overlying waters by diffusion and bioturbation (e.g. *see* Goldhaber et al. 1977). We here focus on two aspects of benthic nutrient recycling in relatively unpolluted sediment from Narragansett Bay: factors determining levels of $CO_2$ and nutrients in pore waters, and the magnitude of benthic fluxes by both advection of water by organisms and simple diffusion (ionic and molecular diffusion) across the sediment–water interface.

Our approach to understanding the relation between benthic fluxes and pore water gradients was to gather sufficient data for estimating both diffusive and advective fluxes and to check our estimates against measured fluxes. (As used here, advective flux denotes transport of dissolved chemical species due to transport of water and sediment by organisms.) Diffusive fluxes were estimated from diffusion coefficients and concentration gradients. Advective fluxes were estimated from laboratory tracer experiments in which we determined the rate of water transport across the sediment–water interface in cores containing an essentially intact benthos. The total benthic fluxes were also measured in the field by bell-jar experiments similar to those of Hale (1974). Good agreement between the measured and calculated (advective plus diffusive) fluxes suggests that this system

[1] Current address: Marine Science Curriculum, 12-5 Venable Hall, University of North Carolina, Chapel Hill 27514.

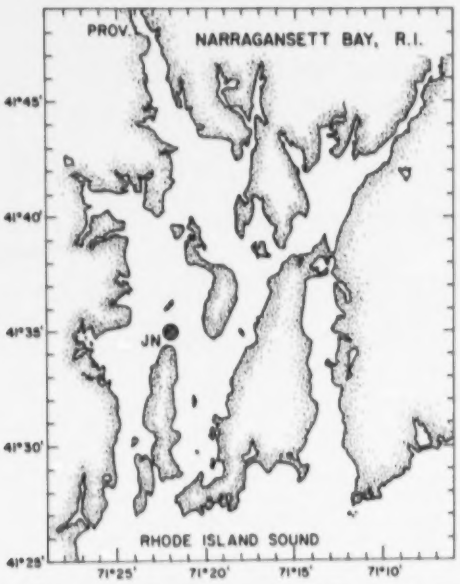



Fig. 1. Location of Narragansett Bay study site JN.

Table 1. Ranges of densities of commonly occurring invertebrates at Jamestown North site from late summer and early fall samples.

| | Density (Individuals $\cdot m^{-2}$) |
|---|---|
| Bivalves | |
| *Nucula annulata* | 800–2,000 |
| *Macoma tenta* | 100–250 |
| *Yoldia limatula* | 50–100 |
| Gastropods | |
| *Nassarius trivittatus* | 100–170 |
| *Turbonilla interrupta* | 500–1,000 |
| Polychaetes | |
| *Nepthys incisa* | 50–140 |
| *Spiochaetopterus oculatus* | 40–100 |
| *Ninoe nigripes* | 50–230 |
| *Maldanopsis elongata* | 30–100 |
| Amphipods | |
| *Unciola irrorata* | 30–120 |
| *Ampelisca abdita* | 30–100 |
| Miscellaneous species | 200–500 |

is well defined. Although the results are directly applicable only to Narragansett Bay, they give some insight into other systems and also provide a basis for estimating the accuracy of benthic fluxes calculated from pore water gradients alone.

We acknowledge the seamanship of Capt. D. Wilcox of RV *Hazel II* and the assistance of A. Soper and divers R. Pavia and P. Benoit. Counting facilities were provided by the Rhode Island Nuclear Science Center. This work was supported by EPA grant R803243.

### *Biology of the infaunal community at the Conanicut Point site*

Our study site (called JN—Jamestown North) was near Conanicut Point, about 0.2 km north of Jamestown Island in Narragansett Bay (Fig. 1). The water is about 6 m deep.

Sediments at this site consist of clayey silts with a small admixture of shells. The infauna belong to the *Nepthys-Nucula* community common to similar sediments and water depths in Long Island Sound to the west and Buzzards Bay to the east. The density of animals is relatively low (Table 1), but bioturbation is sufficient to homogenize the upper 20 cm of sediment so that, in contrast to the findings of Aller and Cochran (1976), we found no stratification of sediments in this layer. The wind-driven circulation may also contribute to the stirring of sediments.

Our picture of bioturbation at the study site consists of two parts. There is a rapidly mixed upper 5–6 cm of sediment occupied by all of the bivalves, gastropods, amphipods, and the polychaetes *Nepthys incisa* and *Ninoe nigripes*. Material in this layer is slowly buried by sediment accumulation and by recycling of sediment from the 15–20-cm feeding depth of *Maldanopsis* re-elevated to the surface as *Maldanopsis* feces. Surface water is probably well mixed into the upper zone, but appears to be introduced to the lower zone at the feeding depth of *Maldanopsis* or at the lower end of a *Spiochaetopterus* tube. The processes operating in the upper 5 cm are probably essentially those described by Aller and Cochran (1976) for Long Island Sound sediments.

Deep burrowers in the area—*Homarus*

*americanus* (lobster) and *Squilla empusa* (mantis shrimp)—move appreciable amounts of sediment in their excavations, but occur in densities so low ($<1 \cdot m^{-2}$) and effect such small overall disturbance as to be safely ignored in considering the genesis of local pore water profiles. The burrowing anemone, *Ceriantheopsis americanus*, lives in a mucus-lined burrow which may reach a meter or more into the sediment, but since we carefully avoided it in field experiments, it, too, may be excluded from consideration.

Figure 2 shows several of the animals and structures commonly seen at the sample site.

*Experimental procedures*

Handheld Plexiglas box cores (2.5 or 7.5 cm thick × 24 cm high × 29 cm wide) were inserted into the sediment by divers, sealed, brought on ship, stored in ice water to minimize further reactions, and returned to the laboratory. Inside a He-filled glove bag at 4°C, 1-cm (or 0.5 cm) layers were scooped from the 7.5-cm-thick core into centrifuge bottles and sealed. The sealed bottles were removed from the glove bag and centrifuged at 4,000 × *g* for 10 min in a refrigerated centrifuge at in situ temperatures to separate pore waters. Recovery of pore water ranged from about 50% of the total water content at the surface to 20% at 1 m. Pore water samples were filtered through 0.4-μm Nuclepore filters; to avoid exposure to air, we used syringes both for introducing the sample and receiving the filtrate.

A long core obtained by divers by inserting 10-cm-i.d. polyvinylchloride (PVC) pipe into the sediment was brought to the laboratory and sampled at selected depths. Pore waters were separated and analyzed by essentially the same procedures used for the box cores.

The concentration of $\Sigma CO_2$ (=total concentration of all species of dissolved oxidized inorganic carbon) was determined immediately after filtration by gas chromatographic analysis of $CO_2$ released by acidifying and purging with He. Filtered and unfiltered samples gave identical results within the analytical precision, estimated to be ±4% (1 $\sigma$) based on replicate analyses of bay water.

Sulfate was measured by $BaSO_4$ precipitation. One milliliter of a 120 mM $Ba(NO_3)_2$ solution spiked with $^{133}Ba(NO_3)_2$ was added to 1 ml of pore water and $BaSO_4$ separated by filtration on a Nuclepore filter. The amount of Ba on the filter was determined by counting $^{133}Ba$ on a Ge(Li) detector coupled to a multichannel analyzer. $S^{2-}$ was measured potentiometrically in cores JN-3, -5, and -6 with a $S^{2-}$ electrode and titration with cadmium. $S^{2-}$ in cores JN-7 and -8 was determined colorimetrically (Cline 1969).

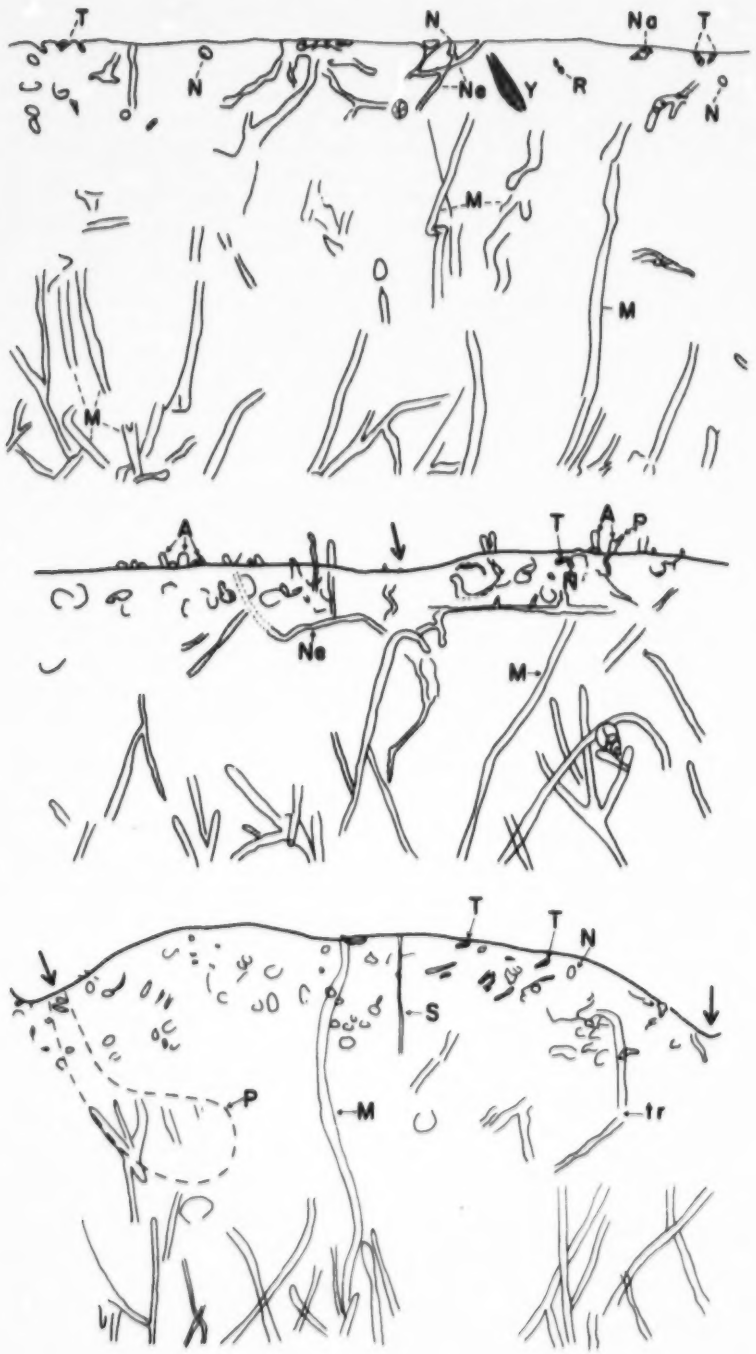
Ammonia was measured by the method of Solórzano (1969). Phosphate and silica were determined by a modified Technicon AutoAnalyzer procedure (Technicon 1973*a*,*b*).

The concentration of dissolved manganese was determined by flameless atomic absorption spectrophometry with either a Perkin-Elmer 503 or 360 AAS with a model 2100 graphite furnace and deuterium arc background corrector. Standards were prepared in Sargasso Sea water.

Calcium : sodium ratios were determined by flame atomic absorption with a Perkin Elmer model 360 AAS, using the method of Hoffman (1975). On the basis of replicate analyses of Narragansett Bay bottom waters and Copenhagen standard seawater, the precision in the Ca:Na ratio is ±0.8% (1$\sigma$).

Porosity was determined from the weight loss upon drying at 110°C. X-radiographs of 2.5-cm-thick box cores were made by placing an 8- × 10-inch (20 × 25 cm) sheet of Kodak industrial type AA film in contact with the rear wall of the box located 86 cm from a 60-kV source and irradiating it for about 2.5 min.

The importance of bioturbation in exchanging bay and pore waters was estimated by bringing three intact box cores to the laboratory and measuring the rate at which $^{22}Na$ ($t_{1/2}$ = 2.64 years) introduced into the overlying water was removed by transport into pore waters and its vertical distribution in the sediment.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Cores were collected in November when the bottom water temperature of the bay was 12°C, stored in the dark in a water bath at 19°C to simulate summer temperature conditions, and kept covered with 6–12 cm of aerated water (light penetration to the bottom at the study site is nearly zero). $^{22}Na$ (along with other radioisotopes) was injected into the overlying water, which was sampled regularly up to the sixth day of the experiment and again at the end of the incubation periods, which ranged from 6 to 13 days. The relative content of $^{22}Na$ in pore water collected from 1-cm intervals in the sediment was measured by gamma-ray spectroscopy and corrected for decay to the time of sampling.

Benthic fluxes were measured in situ using the procedures and PVC chambers (pipe halves with closed ends and a flange at the base) of Hale (1974) and Nixon et al. (1976) or smaller Plexiglas box cores or both. A sample of bottom water was taken by SCUBA divers before the chambers were brought to the bottom. Each chamber covered an area of 0.24 $m^2$ and enclosed 27 liters of water. Alternatively or in addition, box cores each covering an area of 0.0218 $m^2$ were carefully inserted in the mud and the depth of penetration marked. Samples were withdrawn from the enclosures at the beginning and end of the experiment, typically lasting 3 h. Possible flushing of pore water due to creation of a differential pressure across the enclosure wall was obviated by allowing replacement water to enter a semi-isolated antechamber (PVC chamber) or by allowing a flexible diaphragm to collapse during withdrawal (box core).

Data on manganese fluxes used below were given by Graham et al. (1976).

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Fig. 2. Line drawings of X-radiographs. Upper Panel. Tubes of *Maldanopsis elongata* (M) are ubiquitous. Experience with deeper cores indicates that typically increased curvature near bottom is real. Tortuous bends and spirals in some tubes are probably "normal" *Maldanopsis* tubes and are not due to postoccupational disturbance. *Turbonilla* sp. (T) is common and appears to be a deposit feeder, active within top few millimeters. On basis of aquarium observations, those indicated are almost certainly alive and in feeding position. A burrow extends from *Nucula annulata* (N) both toward surface and down a centimeter or so into sediment. An adult *Yoldia limatula* (Y) is present in life position, ventral margin toward viewer. This bivalve is characteristic of site but is not very common. *Retusa canaliculata* (R) and *Nassarius trivittatus* (Na) are also present. Light-colored, dish-shaped depression surrounding *Nassarius* is presumably due to water mixed into sediment as it plows along just below interface (on negative, a mound is evident above this animal). Characteristic Y-shaped burrows of *Nepthys incisa* (Ne) are common within upper 3 cm or so. Many smaller burrows of irregular shape also occur. They are not specifically identifiable but can be ascribed to small bivalves, possibly forams, and small polychaete worms.

Middle panel. Most, if not all, of tubes (A) crossing interface belong to *Ampelisca* (probably *A. abdita*). Tube densities $>3\times10^4 \cdot m^{-2}$ seasonally in certain areas of Narragansett Bay but are rarer and patchy at study site. Tubes typically extend 1–2 cm either side of interface, but appear to be closed at bottom. Several polychaete tubes present in X-radiograph, as at (*P*), are believed to be of *Spiochaetopterus oculatus* (based on common association between *Spiochaetopterus* and *Ampelisca* tube mats). Although not evident in this X-radiograph, its tubes penetrate >20 cm. *Maldanopsis* (M), *Turbonilla* (T), *Nucula* (N), and *Retusa* (R) are also present. Probably all looped-festoon burrows (Ne) are attributable to *N. incisa*, although *Ninoe nigripes* also burrows at this station. Large arrow points to a deep mottled structure, possibly a relict *Cerianthus* anemone burrow.

Lower panel. Prominent *M. elongata* tube (M) extends from sediment surface to >15-cm depth. Tubes of *M. elongata* consist of a hardened sediment ring 1–2 mm thick, covering a parchment tube. Though generally vertical, they often develop curvature at base and may "wag" as animal exploits fresh sediment. Numerous others are present, some evidently sheared, as at tr. Such dismemberment is probably evidence of disturbance in place (*see below*). A *S. oculatus* tube (S) about 1 mm in diameter is readily traced on negative from a few centimeters above interface to at least 6-cm depth. Arrows indicate apparant openings to a shallow U-shaped burrow, probably built by a juvenile *Squilla empusa*. Sediment is less dense along this broad U, and there is a pocket (P) containing what seems to be oriented shell fragments. This feature truncates several *Maldanopsis* tubes. Sheared tubes to right of center also seem to lie within burrowed zone. Between these tubes and pocket, presumed *Squilla* burrow passes out of plane of X-radiograph. There are also several rather deep (6 cm) very thin burrows of unknown origin on each side of the central *Maldanopsis* tube. *Turbonilla* (T), *Retusa*, and *Nucula* (N) are also present.

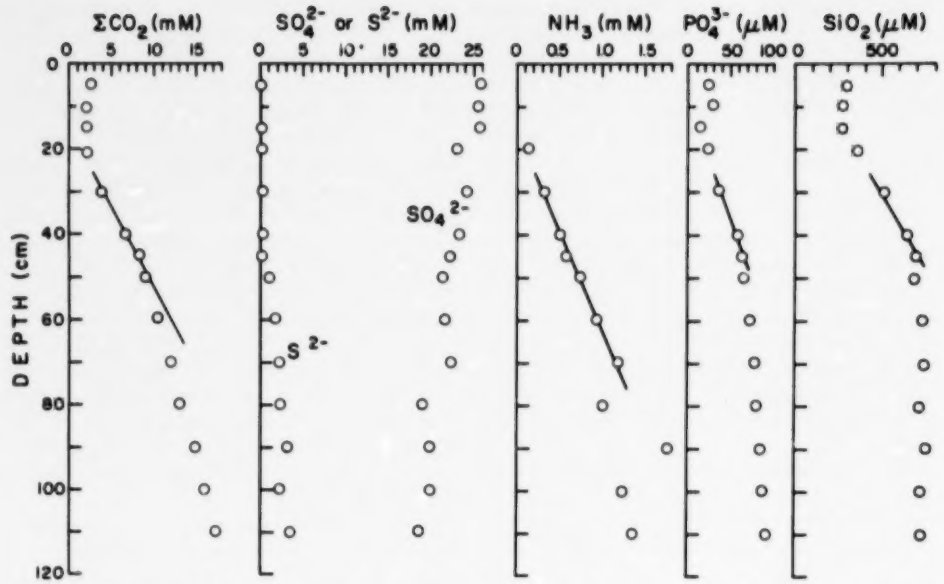


Fig. 3. Concentrations of nutrients vs. depth in pore waters from Jamestown North long core JN-8. Lines are visual estimates of concentration gradient at 25 cm.

*Results and discussion*

*Pore water profiles*—Pore water concentrations of dissolved nutrients and manganese in four box cores and one long core (JN-8) taken in 1975 (JN-3, 3 July; JN-5, 15 July; JN-6, 22 July; JN-7; JN-8, 23 September) are plotted against depth in Figs. 3 and 4. An interesting pattern emerges. Mean concentrations in the top 20 cm are greater than bottom-water values. Bottom-water $\Sigma CO_2$ concentrations, for example, are 2.0±0.1 mM (mean and standard deviation of 11 determinations over a 5-week period) but average about 2.8 mM in the pore water in the short cores. Ammonia values are about 100 μM in the top 20 cm compared with <10 μM in ambient bottom water. Phosphate values range from 20 to 70 μM in the pore water and are <1 μM in bottom waters; $H_4SiO_4$ is about 350 μM in pore waters compared with <10 μM in bottom waters; manganese, which has a concentration of about 0.2 μM in bay waters, reaches 36 μM in pore waters.

The concentrations of the various elements do not show a continual increase with depth in the top 20 cm, but are either nearly constant ($\Sigma CO_2$, ammonia) or show a maximum at about 7 cm. This latter pattern characterizes $H_4SiO_4$ in JN-6 and $PO_4^{3-}$ in all cores. There is also a suggestion that ammonia and $\Sigma CO_2$ decrease slightly below 7 cm (particularly in JN-6).

The data from the long core suggest that below 20 cm the chemical composition varies in a way common to anaerobic sediments (Sholkovitz 1973; Hartmann et al. 1973). In such sediments, diagenesis takes place according to the following reaction (assuming, as a guide, that the C:N:P ratios equal the Redfield ratio: Richards 1965):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \rightarrow 106\ HCO_3^- + 16\ NH_3 + 53\ H_2S + H_3PO_4.$$

In the Jamestown pore waters, $\Sigma CO_2$ rises by about twice the amount of the sulfate decrease and sulfide rises to a concentration of about 2 mM while ammonia

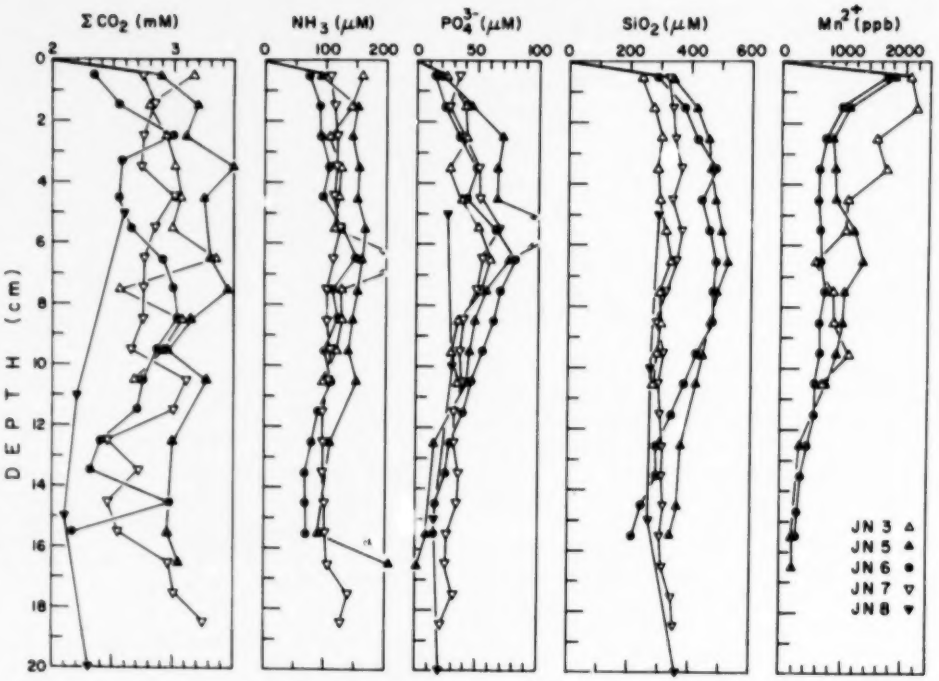


Fig. 4. Concentrations of nutrients and manganese vs. depth in pore waters from Janestown North long core JN-8 and four short cores. Heavier lines show inferred concentration gradients at sediment–water interface.

and phosphate increase with depth. If we neglect any ammonia occupying ion exchange positions (Rosenfeld and Berner 1976), the production of ammonia and phosphate is about that expected from decomposition of organic matter with a C:N ratio of 10 and a C:P ratio of 150, values which may be reasonably ascribed to material decomposing below 20 cm in these sediments. $H_4SiO_4$ increases to about 700 μM at 50-cm depth, where it approaches a constant value.

*Transport of $^{22}Na$ into pore waters*—The results of the tracer experiment are summarized in Table 2 and Fig. 5. The $^{22}Na$ in the overlying water decreased by about 35% in each core during the first week of the experiment. In the core that was incubated for 13 days (T4) there is only a very small additional decrease between day 5 and day 13. This presumably reflects a slowdown or cessation of the activity of organisms after incubation for a week, and the concentrations of $^{22}Na$ after day 5 were not used for the exchange rate calculations. In all cores, the transfer of tagged overlying water down the core is substantial and is far greater than would be predicted from simple diffusion.

The decrease in $^{22}Na$ transfer after 1 week suggests that, even during the first week of the experiment, metabolic activity (and $^{22}Na$ transfer) may have been slower than in the real world. Organisms were still functioning after 1 week, but we are not sure that they were fully active.

*Benthic flux determinations*—Results of benthic flux experiments during summer 1975 are summarized in Table 3. There is satisfactory agreement between

Table 2. Ratio of $^{22}Na$ activity of overlying solution to initial activity of overlying solution as a function of time (in days) after $^{22}Na$ addition.

| Core | 1 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| T1 | 0.88 | 0.79 | 0.79 | 0.74 | 0.66 | |
| T3 | 1.00 | 0.88 | 0.87 | 0.83 | | 0.77 |
| T4 | 0.81 | 0.71 | 0.72 | 0.67 | | |

PVC chamber and box core results. The large standard deviations probably reflect patchiness in the benthic community.

*Nutrient and carbon balance in the pore waters*—Consideration of the pore water $CO_2$ balance shows that most of the pore water metabolic $CO_2$ inventory derives from sulfate reduction.

If we neglect production or consumption of oxidized nitrogen species in the pore waters and assume Redfield stoichiometry for organic matter being oxidized, then we have three overall reactions which may be important in organic matter diagenesis in our cores:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 106\ O_2 \rightarrow 106\ CO_2 + 106\ H_2O + 16\ NH_3 + H_3PO_4;$$

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca^{2+} + 2\ HCO_3^-;$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \rightarrow 106\ HCO_3^- + 53\ H_2S + 16\ NH_3 + H_3PO_4.$$

Consider a closed sediment system, starting with an excess of organic matter, bottom water oxidant, and metabolites ($[O_2] = 0.15$ mM, $\Sigma CO_2 = 2.0$ mM). When all the oxygen is consumed, the $[\Sigma CO_2]$ will rise to 2.15 mM. If 1 mole of $CaCO_3$ dissolves for every mole of metabolic $CO_2$ produced, the $[\Sigma CO_2]$ will rise to 2.30 mM. To ascertain whether this reaction had taken place in our study area, we measured the $Ca^{2+}$:$Na^+$ atom ratio in pore water samples from short cores. The mean and standard deviation were $0.0125 \pm 0.0002$, with identical values for ambient bottom water. Thus $CaCO_3$ dissolution is assumed to be negligible. We estimate that an increase in $\Sigma CO_2$ of some 0.65 mM (2.8–2.15) must result from sulfate reduction, this process being the only plausible additional path for $CO_2$ production. Flux calculations summarized in Table 3 (discussed below), show that this increase was not produced below 20 cm. It follows that most of the ambient $\Sigma CO_2$ in pore waters at depths above 20 cm is generated by sulfate, rather than $O_2$, reduction. Since $O_2$-rich bottom water is presumably mixed into the mud by the activity of animals, we were quite surprised by this result.

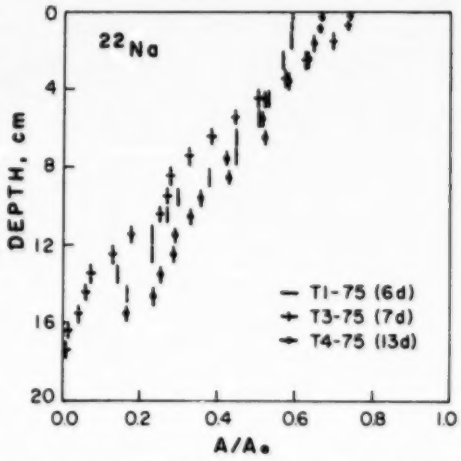


Fig. 5. Results of $^{22}Na$ tracer experiment, showing concentration of $^{22}Na$ in supernatant water and at various depths in cores at end of experiment. T1 was incubated for 6 days, T3 for 7 days, and T4 for 13 days. The e-folding distance for pure ionic diffusion is about 3 cm.

This conclusion applies equally well to an open system. First assume that exchange in Narragansett Bay sediments is dominated by advection (driven by the activity of organisms) and that the process can be described by a simple two-box model, the boxes being bottom water and pore water. In this case, the rate of change of $TCO_2$, assuming oxidation by $O_2$ alone, is

$$\frac{d[TCO_2]}{dt} = Q\hat{K}(\Delta[O_2]) - Q(\Delta[TCO_2])$$

where $Q$ is the water flux between boxes, $\hat{K}$ is the ratio of $CO_2$ production to $O_2$ consumption, and $\Delta[O_2]$ and $\Delta[TCO_2]$ are the concentration differences of $O_2$ and $TCO_2$ between bottom water and pore

Table 3. Summary of fluxes ($\mu mol \cdot cm^{-2} \cdot d^{-1}$) calculated from different approaches.

| | Deep diffusive flux | | | Diffusive flux across interface‡ | | Advective flux across interface | | | Measured fluxes $\bar{x} \pm 1\sigma(n)$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Bio-diffusion model§ | Biopumping model | | | | |
| | $D_s$* | dC/dz† | Flux | dC/dz† | Flux | | Δc‖ | Flux | PVC chambers | | Box cores |
| $H_4SiO_4$ | 0.5 | $1.5\times10^{-2}$ | 0.007 | $6.0\times10^{-1}$ | 0.3 | 2 | 0.4 | 0.3 | 1.2±0.2 | (7) | 1.9±0.2 (2) |
| $NH_3$ | 1.0 | $2.0\times10^{-2}$ | 0.02 | $2.0\times10^{-1}$ | 0.19 | 0.8 | 0.1 | 0.07 | 0.27±0.08 | (15) | |
| $PO_4^{3-}$ | 0.4 | $1.9\times10^{-3}$ | 0.0007 | $5.0\times10^{-2}$ | 0.018 | 0.17 | 0.03 | 0.02 | 0.07±0.02 | (9) | 0.05±0.01 |
| $\Sigma CO_2$ | 0.6 | $3.0\times10^{-1}$ | 0.26 | 1.8 | 0.9 | 6 | 0.8 | 0.6 | 2** | | |
| $Mn^{2+}$ | 0.3 | — | — | 8 | 0.02 | 0.3 | 0.02 | 0.01 | 0.049±0.018 (14)†† | | |

* Diffusion coefficients ($\times10^{-5}$ $cm^2 \cdot s^{-1}$) assumed to be 50% of values at 25°C in deionized water given by Li and Gregory (1974), except for $H_4SiO_4$, which is taken as $0.5\times10^{-5}$ $cm^2 \cdot s^{-1}$, increased from value of $0.3\times10^{-5}$ determined for a deep-sea core at 4°C by Fanning and Pilson (1974).
† In $\mu M \cdot cm^{-1}$.
‡ Values for $D$ same as in deep diffusive flux column.
§ Calculated assuming biodiffusion coefficient of $4\times10^{-9}$ $cm^2 \cdot s^{-1}$.
‖ Mean concentration ($\mu M \cdot cm^{-2}$) in top 20 cm minus concentration in overlying bottom water.
** One 48-h measurement only.
†† Two outlying results, 0.38 and 0.70 $\mu M \cdot cm^{-2} \cdot d^{-1}$, were excluded.

water. The maximum possible value of $\hat{K}$ is that of the organic matter oxidation stoichiometry given earlier, or 1.00. At steady state, taking $\hat{K}$ as 1.00, the above equation yields

$$\Delta[O_2] = \Delta[TCO_2].$$

Next assume that the system is dominated by diffusion, and again assume that organic matter oxidation is by $O_2$ alone. In this case,

$$F_{TCO_2} = D_{TCO_2}\frac{d[TCO_2]}{dz}$$

and

$$F_{O_2} = D_{O_2}\frac{d[O_2]}{dz}$$

where $F$ is the vertical flux of the species considered, $D$ is the diffusion coefficient, and $z$ is depth. Taking $K = 1.00$ and $F_{O_2} = -F_{TCO_2}$ we get, upon integration,

$$\Delta[TCO_2] = -D_{O_2}/D_{TCO_2}\Delta[O_2].$$

In the diffusive case, the change in $TCO_2$ actually is larger than the closed system change by the ratio of the diffusion coefficients or about a factor of 2. In summary, the maximum open system increase in $[TCO_2]$ is 0.15 $mM \cdot kg^{-1}$ in the case of advective exchange and about 0.30 $mM \cdot kg^{-1}$ in the case of diffusive exchange. These values are far lower than the observed increase of 0.8 $mM \cdot kg^{-1}$ and imply that most of the steady state excess of pore water $TCO_2$ is produced by $SO_4^{2-}$ reduction.

Concluding that most of the pore water standing crop of metabolic $CO_2$ derived from sulfate rather than $O_2$ reduction led us to ask this question: in the integrated entire sediment column, does the *rate* of sulfate reduction exceed the rate of $O_2$ reduction? In other words, does most metabolism proceed by $O_2$ or by sulfate reduction? Data given below indicate that the flux of $\Sigma CO_2$ from sediments to bottom water is 2 $\mu M \cdot cm^{-2} \cdot d^{-1}$. There are no constraints which rule out the possibility that sulfate reduction can account for most of this flux. If $O_2$ reduction in fact competes with sulfate reduction and if transport takes place by diffusion, then we can calculate that the gradient $d\Sigma CO_2/dz$ in pore waters at the sediment–water interface must be about 6 $mM \cdot cm^{-1}$ down to a depth of no more than a few hundredths of a centimeter, at which point all $O_2$ would be consumed and the $\Sigma CO_2$ concentration, now increasing as a result of sulfate reduction, would rise more slowly. We see no way of ascertaining if such a gradient exists. The sediment–water exchange model outlined below assumes that the gradient in $\Sigma CO_2$ is about a factor of three lower, which implies that most organic matter oxidation is by sulfate reduction. However, this is based on a guess about the shape of the

$\Sigma CO_2$-depth curve in the top centimeter and may be wrong.

All but two phosphate values fall between 10 and 70 $\mu$M and cluster around 30 $\mu$M. A typical $\Sigma CO_2/[PO_4^{3-}]$ value for the top 20 cm is thus about (2.8–2.0 mM)/30 $\mu$M = 27:1, which value is about a factor of four lower than that expected for marine phytoplankton and other tissue reaching Narragansett Bay sediments. $[PO_4^{3-}]$ does not follow $[\Sigma CO_2]$ nearly as closely as ammonia does. We interpret the low C:P ratio and the lack of coherence between $PO_4^{3-}$ and $\Sigma CO_2$ as indicating that most of the $[PO_4^{3-}]$ in pore waters in the top 20 cm derives from dissolution of inorganic compounds, presumably ferric phosphates (Bricker and Troup 1975), in the sediments.

The $H_4SiO_4$ concentration increases rapidly beneath the interface and reaches a broad maximum at about 7 cm then decreases (Fig. 4). As seen in the long core (Fig. 3), the concentration again increases over the 20–40-cm-depth interval to a level about twice that in the disturbed zone. The higher silica concentration in pore waters than in bottom waters presumably reflects dissolution of diatoms. The shallow minimum in silica concentration appears to result from the irrigation activities of polychaete worms. Grundmanis and Murray (1977) noted a similar phenomenon.

Dissolved manganese reaches a maximum within the top centimeter, then rapidly decreases with depth (Fig. 4). A likely explanation for this is the reduction of manganese hydroxyoxides to soluble Mn (II), perhaps by $HS^-$ produced during bacterial sulfate reduction (Morgan 1967). There must be net fluxes of manganese from the top centimeter both upward into the overlying water and downward into the sediment. The identity of the accumulating solid phase implied by the downward flux is unknown.

### *Calculating benthic fluxes from pore water concentrations*

Dissolved chemicals transported across the sediment–water interface originate either by organic matter decomposition within the top 25 cm of the sediment column or by decomposition at greater depths and diffusion into the top 25 cm. Transport of dissolved chemicals across the interface is driven by two processes: advection of water by animals and simple diffusion. Since examination of the biota of our study site showed that the activity of organisms is concentrated in the upper 20 cm, we assume that at greater depths advection is negligible.

Advection may be viewed either as a basically random process, in which organisms move water through the sediments isotropically (here termed "biodiffusion"), or a basically ordered process, in which organisms direct the transport of material between the sediment and overlying water (here termed "biopumping"). We model transport of metabolites in two ways. In both models we assume that metabolites released below 25 cm are transported into the zone of bioturbation by simple diffusion, but in the first we assume that metabolites are transported across the sediment–water interface by biodiffusion (which includes simple diffusion but is dominated by animal-driven advective transport of water) and in the second that metabolites are transported across the sediment–water interface by both simple diffusion and biopumping. Flux estimates from both models are given below.

*Calculation of the deep diffusive flux*—The flux of dissolved chemicals across the 25-cm-depth contour is equal to the concentration gradients at this depth times the apparent diffusion coefficients (Li and Gregory 1974). Concentration gradients are assumed to be values indicated by the solid lines below 25-cm depth in Fig. 3.

Apparent diffusion coefficients are difficult to estimate in the absence of experimental determinations. The bay bottom-water temperature during the summer months was typically 20°C. We estimate that apparent diffusion coefficients are half the values of diffusion coefficients in deionized water at 25°C (as summarized by Li and Gregory). The $D_a$ thus calculated for $SO_4^{2-}$ is $5.3 \times 10^{-6}$

$cm^2 \cdot s^{-1}$, which can be compared with the value of 4.0 determined experimentally for Long Island Sound sediments at about 20°C by Goldhaber et al. (1977). At the sediment–water interface in Narragansett Bay, where the water content is higher than that of average Long Island Sound sediments (0.60% by weight vs. 0.45%), our estimated $SO_4^{2-}$ diffusion coefficient appears quite reasonable. At depth in Narragansett Bay sediments, where the water content is about the same as in Long Island Sound, we may be overestimating $D_a$ by about 25%.

The dominant $CO_2$ species is $HCO_3^-$. We assume that any adsorbed component is retained on the clay during squeezing, and that $D_a$ values estimated above need not be further corrected for adsorption. We make analogous assumptions for other species.

Deep diffusive flux calculations using these values are summarized in Table 3.

*Simple diffusive fluxes across the sediment–water interface*—Concentrations generally rise so steeply at the sediment–water interface that our closely spaced sampling is insufficient for accurately determining the gradients here. Estimated concentration gradients at the interface are given as heavier lines in Fig. 4. Diffusion coefficients are estimated as outlined above. The simple diffusive fluxes across the sediment–water interface are equal to the product of the apparent diffusion coefficient and the concentration gradient. Calculated values are given in Table 3.

*Advective fluxes across the sediment–water interface*—For both models used to calculate advective fluxes across the interface, data from the $^{22}Na$ tracer experiment are used to calculate parameters describing the effects of advection on sediment–water exchange. In the biodiffusion model we assume that the advection is completely random and can be described mathematically by diffusion equations. An apparent diffusion coefficient, which we term the "biodiffusion coefficient" ($D_B$), can be estimated by Crank's (1970) treatment of solute diffusing from a well stirred solution of limited volume into a porous medium. Data used in the calculation are given in Table 4. From the total loss of $^{22}Na$ from overlying water during each of the three experiments, a value of $D_B$ of $4.0 \pm 2.7 \times 10^{-5}$ $cm^2 \cdot s^{-1}$ is estimated. Note that the biodiffusion coefficient incorporates the effects of simple diffusion.

In our biopumping model, organisms are assumed to pump water between various depths in the sediment and the overlying water. The data from the $^{22}Na$ experiment are used to obtain a minimum estimate of the "biopumping rate"—the volume of water exchanged each day per unit surface area between the pore water and the overlying solution. Since we did not measure transport to various depths in the sediment column as a function of time, our data are inadequate to allow rigorous calculation of the biopumping rate. To make a first-order estimate we make a drastic assumption—that the exchange rate is constant throughout the length of core sampled. We further ignore transport of $^{22}Na$ into pore waters by simple diffusion (*see* Luedtke and Bender 1979), which in any case is very slow since biological mixing eliminates the large concentration gradients required for rapid simple diffusion. The process can then be treated as an exchange between two well mixed reservoirs: pore water and overlying water. The decrease of $^{22}Na$ in the supernatant solution is described by

$$\frac{dC_s(t)}{dt} = -KC_s(t) + K\frac{V_s}{V_p}C_s(0) - K\frac{V_s}{V_p}C_s(t)$$

where $C_s(0)$ is the normalized $^{22}Na$ concentration in overlying solution at time $t = 0$, $C_s(t)$ the normalized $^{22}Na$ concentration in overlying solution at any time $t$, $K$ the exchange constant, $V_s$ the volume of overlying solution, and $V_p$ the volume of pore water. The first term on the right refers to pumping of $^{22}Na$ into the pore water, and the next two terms refer to pumping out of the pore water. The pore water $^{22}Na$ concentration is calculated from the $^{22}Na$ loss of the supernate times

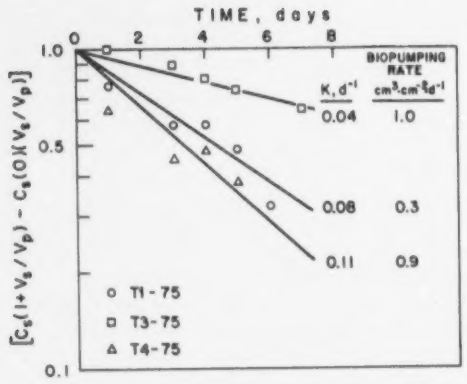


Fig. 6. Change in $\ln\left[C_s\left(1+\frac{V_s}{V_p}\right)-C_s(0)\left(\frac{V_s}{V_p}\right)\right]$ as a function of time after $^{22}Na$ addition to overlying water. Values of $K$ and biopumping rate are derived from slope of lines (terms explained in text).

the ratio of supernate to pore water volume. The solution to the equation is

$$C_s(t)=\frac{1}{\left(\frac{V_s}{V_p}+1\right)}\left\{\frac{V_s}{V_p}C_s(0)+\exp\cdot\left[(-Kt)\left(\frac{V_s}{V_p}+1\right)\right]\right\},$$

which can be rearranged to

$$\ln\left[C_s(t)\left(1+\frac{V_s}{V_p}\right)-\frac{V_s}{V_p}C_s(0)\right]=-K\left(1+\frac{V_s}{V_p}\right)t.$$

$K$ is equal to that fraction of the supernate that must be pumped across the sediment–water interface to account for the observed decrease of $C_s$ with time. The biopumping rate is then given by the product of $K$ and the volume of supernate per square centimeter of sediment. The values of $K$ and the biopumping rate are estimated from the slope of the lines shown in Fig. 6 and summarized therein. The estimated biopumping rate is $0.7\pm0.4$ $cm^3\cdot cm^{-2}\cdot d^{-1}$.

Values of the advective flux calculated from the biodiffusion and the biopumping models are given in Table 3. The biopumping flux is the product of the average increase in the concentration of constituents in the pore water relative to bottom water times the biopumping rate ($0.7\ cm^3\cdot cm^{-2}\cdot d^{-1}$). The calculated biopumping flux does not incorporate transport across the sediment–water interface by simple diffusion.

These results, together with experimental benthic flux results, are given in Table 3. There are several indications that the biodiffusion model is not a satisfactory representation of reality. First, the decrease in $^{22}Na$ activity with depth in the sediments is linear, rather than exponential as would be expected from a random process. For a diffusionlike process to produce linear $^{22}Na$ concentration gradients, the biodiffusion coefficient would have to increase with depth, which seems most unlikely. Even more damaging to the biodiffusion model are the observations of constant pore water concentrations (or even maxima) in the top 20 cm. Where there are no positive concentration gradients, random processes (which produce fluxes toward the interface only along positive concentration gradients) cannot transport metabolites toward the sediment–water interface.

One obvious objection to the biopumping model is that the calculation of biopumping rate assumes that pumping proceeds at equal rates at all depths above 20 cm. This is almost certainly not true, but the problem can be resolved only by a much better understanding of the behavior and vertical distribution of animals, especially the irrigation and feeding activities of *Maldanopsis elongata* at this site, along with data which give the $^{22}Na$ distribution in pore waters as a function of time. Our calculated biopumping rates should be considered lower limits to the true values, since our model does not consider the possibility of rapid exchange between the bottom water and the top few centimeters of pore water.

Nevertheless, we regard the biopumping model as a satisfactory starting point. The type of transport involved in the biopumping model is evidently a profit-

Table 4. Results for calculating biodiffusion coefficients, $D_B$, from decrease in $^{22}Na$ content of supernate. $D_B$ calculated for each experiment from fraction of initial $^{22}Na$ remaining in overlying water on fifth day of experiment.

| | $T$ (d) | $A$* (cm) | $L$† (cm) | $M_T/M_\infty$‡ | $1/(1+\alpha)$§ | $(D_eT/L^2)$‖ | $D_B$ $10^{-6}$ cm$^2$·s$^{-1}$ |
|---|---|---|---|---|---|---|---|
| T1 | 5 | 12.1 | 17 | 0.518 | 0.496 | 0.29 | 6 |
| T3 | 5 | 6.4 | 18 | 0.258 | 0.662 | 0.11 | 0.9 |
| T4 | 5 | 8.5 | 14 | 0.621 | 0.536 | 0.35 | 6 |

* Height of solution.
† Height of sediment column.
‡ Total amount of solute in sediment at time $T$/total amount of solute in sediment at equilibrium.
§ $\alpha = A/L\phi$ = ratio of volume solution to volume pore water; $\phi$ = porosity.
‖ Calculated from graphical solution of Crank (1970) for uptake by a plane sheet from a stirred solution of limited volume.

able way for some benthic organisms to expend energy; thus this model may be more realistic than the biodiffusion model. It is also attractive because it can explain the minima sometimes found in nutrient concentrations between 5 and 20 cm. The biopumping model predicts that the steady state concentration of a dissolved chemical equals the decomposition rate at a given depth divided by the rate at which water is pumped to that depth. Both rates probably generally decrease with depth. However, if the decomposition rate decreases more rapidly than the pumping rate, the concentration of metabolites will actually decrease with depth. Below about 25 cm, pumping is assumed to cease; hence below this depth the dissolved chemical concentration can once again increase.

*Relative fluxes due to different processes*—Diffusive fluxes of constituents across the sediment–water interface are compared with biopumping fluxes in Table 3. Our calculations indicate that diffusion transports ammonia, $\Sigma CO_2$, and $Mn^{2+}$ faster than biopumping, and phosphate and $H_4SiO_4$ at the same rate as biopumping. This is a remarkable result: even at this site of high benthic activity diffusion is as important as the activity of organisms in transporting metabolites to the overlying waters. Presumably this is because most nutrient release to pore waters takes place in the upper centimeter of the sediment. At this depth, diffusion to overlying waters is so rapid that it, rather than pumping, is the dominant pathway of release.

The sum of the biopumping and diffusive fluxes agrees with measured fluxes to within a factor of two or better. This is gratifying and leads us to conclude that the system is reasonably well characterized.

The deep diffusive fluxes are about 1% of the benthic fluxes for $H_4SiO_4$ and phosphate and 7% of the benthic fluxes for ammonia and $\Sigma CO_2$. These latter values indicate that metabolism below 20 cm is a small but significant fraction of the total metabolism in the sediment column.

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